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The
Electrolytic Deposition
of
Antimony

THESIS

Presented to the Faculty of the Department of
Philosophy of the University of Pennsylvania
in Partial Fulfilment of the Requirements for the Degree of Doctor
of Philosophy

BY
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THE ELECTROLYTIC DEPOSITION OF ANTIMONY.

The developments in the field of electro-chemistry have reached a point where the continued isolation of electrolytic methods of analysis from the usual gravimetric and volumetric processes should cease. That such isolation exists very generally is unquestioned, and is due primarily to two causes: first, the lack of a widespread knowledge of the technique of electrolytic methods; and second, to a natural tendency by electrochemists to endeavor to make electro-chemical analysis as complete in itself and as independent of ordinary analytical procedure as possible. From the viewpoint of technical and general analytical chemistry this is unfortunate, since the latter will be best advanced by the freest use and combination of every possible resource, chemical, physical or electrical, which is available. A soluble substance may be removed from a precipitated solid by filtering, or by electrolysis. The discussion of whether the latter is an "electrolytic separation" is purely academic from the standpoint of general analysis. The important question is, which, in a particular instance, is the most efficient?

Having regard to electrolytic procedure as an aid rather than a rival of existing methods, it is evident that the most desirable points of development for electrolytic methods are where the existing methods are most unsatisfactory or difficult. Therefore the problem of the separation and determination of antimony and tin by electrolytic methods forms a very natural point of attack.

The rapid electrolytic deposition of antimony from an alkaline electrolyte of sodium sulphide, potassium cyanide and sodium hydrate as carried out in this

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laboratory by Dr. Franz F. Exner and later by Dr. Julia Langness affords a method for the estimation of antimony which in the hands of an experienced operator has no superior for ease, rapidity and accuracy.

Tin may also be very satisfactorily deposited as metal from the solution of its sulphide in ammonium polysulphide.

When both antimony and tin are present together, however, neither of these methods is available, as tin is incompletely deposited from a sodium sulphide electrolyte, and metallic antimony is appreciably soluble in ammonium sulphide. These facts have seriously limited the usefulness of the electrolytic methods mentioned above for practical analytical purposes.

With a view therefore of finding an electrolytic process readily applicable in the determination of antimony or tin, when both are present, the following work was undertaken.

The behavior of a large number of electrolytes with respect to antimony and tin has been studied. Those electrolytes which gave indications of availability have been more carefully tested over a wide range of conditions, e. g., voltage, current density, addition of various salts, temperature range, form and size of electrodes and rates of rotation of anode or cathode.

The description of the experimental work is arranged under the headings of the various electrolytes studied.

I. Ammonium Lactate Electrolyte.

The apparatus was of the usual type, consisting of a 150 cc. platinum basin, sand blasted inside, for a cathode, an anode of heavy platinum wire with a flat spiral tip, adjusted about 1 cm. from the bottom of the cathode dish, and rotated at any desired speed by a motor controlled by series resistance, and two glass cover plates, notched at the center for the admission of the anode. The electrolyte was made up to 125 cc. in volume which covered a cathode surface of 100 square cm.

About fifteen determinations were made upon antimony chloride. The voltage, current density, rate of rotation of anode, concentration of ammonia and of lactic acid were systematically varied. The deposits were spongy and non-adherent except for the following conditions.

Ten cc. of lactic acid diluted to 125 cc. and made barely ammoniacal gave an adherent velvet deposit of antimony with a high rate of rotation of anode. The current was 3.5 volts and 0.5 ampères $= N.D._{100}$. In one half hour the bulk of 0.2 of a gram of antimony was deposited, but the deposition was never quantitative, the results being from 2 to 20 milligrams low. The addition of 0.5 gram of ammonium nitrate gave a preliminary coating of antimony like polished nickel in appearance. A black deposit followed, which was not complete. Slightly better results were obtained in the presence of potassium sulphate.

The failure to deposit the last traces of antimony was attributed to the following causes:

First. The formation of decomposition products in the course of electrolysis. An odor like that of acetamide always appeared. That the decomposition products formed, exercised a retarding influence upon the deposition of antimony was indicated by the following experiments. An electrolytic bath of ammonium lactate was made up in the usual manner, and a current allowed to pass for fifteen hours before the addition of 0.2 gram of antimony chloride. No deposition could be obtained at any voltage. Then to a perfectly fresh bath of ammonium lactate, 5 milligrams of antimony chloride wers added and a deposit was obtained in five minutes.

A second cause for failure was found when later work showed that the presence of free ammonia in any electrolyte prevents the complete deposition of antimony. Hence the ammonium salt of any weak acid will prove useless unless the last traces of free ammonia can be removed by heating or otherwise before the completion of electrolysis.

II. AMMONIUM POLYSULPHIDE ELECTROLYTE.

The fact that the deposition of antimony was incomplete from an ammonium sulphide bath, and complete from a sodium sulphide bath, suggested that the cause was in the different concentration of hydroxyl ions. Therefore the addition was made to the ammonium polysulphide bath of sodium carbonate, barium hydrate and calcium hydrate respectively.

Ten cc. of antimony chloride were precipitated and redissolved in the least possible quantity of ammonium polysulphide. This was diluted to 110 cc. with water and 20 cc. of saturated barium hydrate were added. The anode was rotated with moderate speed. The voltage was 3.5 and amperage 0.5 $N.D._{100}$. The deposits were brilliant and metallic in character, like polished platinum, very unlike the usual dark electrodeposits of antimony. The greater part of 0.2 gram of antimony was deposited in 30 minutes. Similar brilliant metallic deposits were obtained by the addition of 20 cc. of saturated calcium hydroxide solution or 1 gram of sodium carbonate to the ammonium sulphide bath.

The deposits, however, were not quantitative by several milligrams. Slight differences in the concentration of ammonia and ammonium polysulphide were found to have very disturbing influences upon the course of the electrolysis. Particularly was this true of the amount of sulphur dissolved in the ammonium polysulphide. As sodium carbonate was preferable to barium or calcium hydrate as an addition reagent, a careful investigation was made of the effect upon the deposition of antimony of the three substances: sodium carbonate, ammonium polysulphide and ammonia respectively.

First the addition of increasing amounts of sodium carbonate to the ammonium sulphide electrolyte was tried.

In each of the following series, 10 cc. of antimony chloride, containing 0.2424 grams of antimony were dissolved in the amount of ammonium polysulphide, diluted to 125 cc. and electrolyzed at 3.5 volts and 0.5 ampères $N.D._{100}$, 500 anode revolutions per minute. The electrolysis was continued for one hour under constant conditions except for the addition of the stated amounts of sodium carbonate. The deposits were washed with water, alcohol and ether and dried and weighed.

Wt. Na_2CO_3.	Wt. Sb.
0.5 gram	0.2394 gram
1.0 gram	0.2390 gram
2.0 grams	0.2369 gram
4.0 grams	0.2355 gram
6.0 grams	0.2346 gram

A steady decrease in the rate of deposit was therefore found for increasing concentration of sodium carbonate. This may be due to the increased amount of free ammonia.

The following standard solutions were then prepared: (1) 500 cc. of antimony chloride in hydrochloric acid solution containing 0.2384 grams of antimony in 10 cc. (2) A saturated solution of potassium cyanide. (3) A saturated solution of sodium sulphide, sp. gr. 1.175, freshly prepared and free from polysulphide. (4) A saturated solution of ammonium polysulphide prepared by saturating ammonia with hydrogen sulphide and flowers of sulphur. (5) A saturated solution of ammonium sulphide. (6) A solution of sodium carbonate containing one gram of the salt in 10 cc. (7) Solution of 25 per cent sodium hydroxide.

Determinations of the standard antimony chloride solution were made by the regular sodium sulphide and potassium cyanide electrolyte as follows:

Ten cc. of antimony chloride were measured from a calibrated pipette into the platinum cathode dish. Just enough sodium hydroxide was added, with stirring, to nearly redissolve the precipitated antimony. Fifteen cc. each of saturated potassium cyanide and sodium sulphide were added and the solution diluted to 125 cc. The anode was rotated at about 500 revolutions per minute. For the first five minutes electrolysis was conducted at 2.5 volts and 1 ampère = $N.D._{100}$. Then three volts and two ampères for forty-five minutes. A polished, adherent, slate colored deposit is formed. When finished, the electrolyte is removed by a syphon, fresh water being added meanwhile. The current is then switched off and the deposit washed with alcohol and ether, and dried at 100°.

Duplicate determinations gave the following results:

	Wt. Sb.
(1)	0.2384 gram
(2)	0.2385 gram

The same method was now used with the addition of stated amounts of sodium carbonate.

Wt. Na_2CO_3 in electrolyte.	Wt. Sb.
0.5 gram	0.2386 gram
1.0 gram	0.2383 gram
1.5 grams	0.2382 gram
1.5 grams	0.2380 gram

This would indicate that the sodium carbonate in small concentrations does not exert any retarding influence in the deposition of antimony. In larger amounts there appears to be a slight effect.

Upon the addition of 10 cc. of ammonia to the sodium sulphide-potassium cyanide bath, a distinct loss was apparent.

	Wt. Sb.
(1)	0.2377 gram
(2)	0.2377 gram

The combined addition of 10 cc. of ammonium hydroxide and 1 gram sodium carbonate gave the weight of antimony, 0.2366 gram. The addition of 10 cc. of saturated colorless ammonium sulphide gave a still lower value of 0.2355 gram.

A platinum dish containing a deposit of metallic antimony was washed with colorless ammonium sulphide. Upon reweighing, it had lost 1.2 milligrams. The dish was now filled with ammonium sulphide and for ten minutes a current was passed in while the dish was made the cathode. In spite of the opposing voltage, 1.6 milligrams of antimony went into solution. By reversing the current it was found possible to plate the cathode from metallic antimony upon the anode, using pure ammonium sulphide as the electrolyte.

Metallic antimony is therefore appreciably soluble in colorless ammonium sulphide. This, and not the lower hydroxyl concentration, explains the incomplete deposition from ammonium sulphide solution. It seemed therefore that while the greater part of the antimony could be deposited as a brilliant white metal from an ammonium polysulphide electrolyte, quantitative results would not be possible unless at the end of the electrolysis the concentration of ammonia and ammonium sulphide could be made negligible.

To effect this result, the electrolysis of antimony chloride was carried out with ammonium sulphide at boiling temperature. The ammonia and ammonium sulphide were thus removed or oxidized to ammonium sulphate as the antimony was deposited. The deposits were of polished white metal. The results were quantitative. In the early part of the electrolysis, much sulphur separates upon the anode. This is subsequently oxidized and the free ammonia is volatilized, leaving a clear, colorless bath free from antimony. A highly essential condition to the satisfactory progress of the electrolysis is the proper initial concentration of the ammonium polysulphide.

This must have enough sulphur in it so that not more than 5 cc. of the solution is required for the solution of 0.2 gram of antimony in the form of the chloride solution.

A standard solution of ammonium polysulphide which could be easily duplicated was prepared.

Solution A.—Saturate concentrated aqueous ammonia with hydrogen sulphide in the presence of excess of powdered sulphur. Filter off excess of sulphur after long shaking.

Solution B.—Saturate a concentrated ammonia solution with hydrogen sulphide.

One part of solution *A* is added to six parts of solution *B* for final use.

The ammonium polysulphide so prepared is added dropwise to the antimony chloride solution in a small covered beaker until the latter forms a clear solution.

This is then washed into the platinum dish, diluted to 125 cc. and electrolyzed at the boiling point, with an initial voltage of 3.5 and 1 ampère $= N.D._{100}$. As soon as the amperage falls by exhaustion of the bath, the voltage is raised to 4 volts. Time 1 hour. Rotation of anode, 400 revolutions per minute.

Wt. Sb found by Na_2S–KCN method	0.2385 gram	(1)
Wt. Sb found by $(NH_4)_2Sx$ method	0.2386 gram	(2)
Wt. Sb found by $(NH_4)_2Sx$ method	0.2384 gram	(3)

The deposition of antimony from an ammonium sulphide electrolyte has two points of interest. One is the metallic appearance and character of the deposit, which may prove suitable for electro-plating.

The second is the fact that it makes it possible to determine total tin and antimony in the form of their sulphides quantitatively in the same electrolyte. It remains to separate and determine one of these two metals in the presence of the other to provide a complete analytical method.

Because of the metallic character of the deposit, an attempt was made to determine antimony in the mercury cup with ammonium sulphide electrolyte. It was found that antimony up to 0.1 gram in weight could be amalgamated with mercury and weighed, when a rotating anode was used and the E. M. F. was kept below 3.5 volts. Time required, one hour. The surface of the mercury seemed eventually to become saturated and then a loose powdery deposit was formed which did not amalgamate. It is possible that with larger quantities of mercury and a means of agitating the same, a successful method could be developed.

III. TARTRATES AND TARTARIC ACID ELECTROLYTES.

In the search for a separation of antimony and tin, a variety of electrolytes was considered. The discovery of the retarding effect of ammonia led to a trial of sodium and barium lactates instead of ammonium lactate, but with the former the deposits were loose and worthless.

It was found that tin in the stannic condition was not deposited from sodium or ammonium tartrate solutions, while antimony could be (under certain conditions) deposited in an adherent and weighable form. Weak and concentrated solutions of sodium and potassium and ammonium tartrates were carefully investigated, but it was found that, as in the case of the lactate solutions, the last traces of antimony could never be quantitatively removed.

Saturated solutions of tartaric acid were found to give firm graphite-like deposits of antimony with less than two volts, but were not quantitative.

To determine whether interfering decomposition products were formed in the course of electrolysis, 20 cc. of saturated tartaric acid solution were diluted to 50 cc. with water and electrolyzed for one hour, at 5 volts and 1 ampère. To this and to a similar un-electrolyzed bath, antimony chloride solution was added drop by drop till deposition occurred. No difference was observed. More than 15 milligrams of antimony were added before any deposition occurred in either case. Since the bath seemed to remain constant an attempt was made to "saturate" a tartaric acid bath with antimony by adding a small amount of antimony sulphide and electrolyzing till no more antimony would deposit. This bath was then to be used for the determination of a regular sample of antimony and tin. It seemed from the preliminary work that conditions might be standardized rigidly enough to permit of a determination of antimony in the presence of tin in this manner. The difficulties and obvious objections to such a procedure, however, led to the search for more promising electrolytes.

IV. The Alkaline Earth Sulphides as Electrolytes for Antimony.

Solutions of the hydrosulphides of magnesium, calcium and barium were formed by passing hydrogen sulphide through saturated solutions of the hydroxides in presence of excess of the solid hydrate or oxide and the relative solubilities of the sulphides, arsenic, antimony and tin were roughly determined. Barium hydrosulphide alone dissolved a sufficient amount of antimony sulphide to appear practicable as an electrolyte, the others required too bulky a solution for work in platinum vessels. With the use of barium hydrosulphide, the formation of solid barium carbonate in the vessels during electrolysis proved troublesome.

It was found that a simple qualitative separation of antimony and tin sulphides consisted in adding to them cold saturated barium hydrate in large excess. The antimony sulphide readily dissolved upon stirring, leaving the bulk of the tin sulphide to be filtered out. Upon boiling the filtrate, the slight amount of tin present was quantitatively precipitated as stannic hydroxide. This has some advantages over the more usual separation of these sulphides by calcium hydroxide. The antimony sulphide is more soluble, the tin sulphide is more insoluble and is more promptly precipitated upon boiling. Where large amounts of both tin and antimony are present, a rough qualitative separation can be obtained with cold solutions.

Since it is desired to avoid the removal of tin from antimony by a tedious process of filtration and washing, it seemed that to remove the antimony, by electrolysis, from the precipitated stannic hydroxide would afford the best prospect of a convenient and simple separation. Satisfactory deposits of antimony were not obtained with magnesium hydrosulphides. Barium salts were objectionable because of the formation of solid carbonate. The remainder of the work was therefore devoted to the problem of securing quantitative deposits of antimony from electrolytes of calcium hydroxide and sulphide, in the presence of and free from tin.

The initial objection to calcium hydrosulphide as an electrolyte had been the large bulk of solution required to dissolve a small amount of antimony sulphide. It appeared, however, that the solution of antimony sulphide is largely due to the presence of calcium sulphide (CaS) in the solution which seems to form a weak complex salt with antimony sulphide (Sb_1S_0). This double salt is so weak that it is broken down by excess of hydrogen sulphide with the partial reprecipitation of antimony sulphide. This is indicated as follows:

To a saturated solution of calcium hydrate add antimony trisulphide in excess. Heat the solution and pass in hydrogen sulphide. The excess of solid antimony sulphide will go into solution, clear and colorless. Cool the solution and again saturate with hydrogen sulphide and solid antimony sulphide will be precipitated. Again boiling off the excess of hydrogen sulphide will give a clear solution. The most probable explanation of this behavior is that given above. In a solution of calcium hydrate, saturated at boiling temperature with hydrogen sulphide, antimony sulphide is sufficiently soluble so that the difficulties of too bulky an electrolytic bath are removed. An attempt was made to determine the best conditions for depositing antimony from a calcium sulphide electrolyte. The apparatus used for the earlier work was that already described, a platinum dish as cathode, a rotating spiral anode and about 125 cc. of electrolyte covering 100 square cm. of cathode. A standard antimony chloride solution in hydrochloric acid was prepared. Merck's calcium oxide was powdered and the desired amounts added in dry form to the bath. The presence of a small amount of ammonium polysulphide seemed to favor the formation of a brilliant white deposit. Therefore the following procedure was tried.

Ten cc. of antimony chloride solution were neutralized in a beaker with powdered lime. Ammonium polysulphide was added in sufficient amount to get the antimony in solution. A slight excess of powdered lime was then added, the whole diluted to 100 cc. and boiled until the excess of ammonia was removed. The solution was then put in the platinum dish and electrolyzed over a low flame at boiling point. The most successful results were obtained with an initial E. M. F. of 3.0 to 3.25 volts and a current of 0.3 ampère $=\mathrm{N.D.}_{100}$. for the first ten minutes, then 3.5 volts and 0.4 ampères. In thirty minutes the current would drop to 3.0 volts and 0.4 ampères and in forty-five minutes it would rise to 3.5 volts and 2.5 ampères. After seventy-five minutes, the current was raised for fifteen minutes to 4 volts and 0.4 ampères. Total time, one and a half hours. The rotation of the anode was as rapid as possible without spilling the electrolyte. The deposit was washed with water and then with a solution of 4 cc. of concentrated hydrochloric acid in 400 cc. of water and dried at 100° C. The deposits were brilliant and adherent and no sulphur remained upon the anode at the end of the electrolysis. The results, however, were high unless extreme care was taken, as a white deposit of calcium hydrate or carbonate tended to form in a small spot in the center of the dish and the removal of this with acidulated water sometimes caused bits of antimony to break off. After much practice, some fairly concordant results were obtained, e. g.:

	Gram
Wt. Sb by KCN and Na_2S method	0.2146
Wt. Sb by KCN and Na_2S method	0.2148
Wt. Sb by KCN and Na_2S method	0.2151
Wt. Sb by CaS and $(NH_4)_2S_x$	0.2149
Wt. Sb by CaS and $(NH_4)_2S_x$	0.2150

To avoid the difficulty of solid particles lying upon the bottom of the dish and becoming embedded, a beaker was used in which a double gauze platinum disc was rotated as cathode, a platinum wire being introduced and coiled above the disc as anode.

The electrolytic solution of antimony was prepared as before in the beaker and the electrodes then introduced. The electrodes were separated so that a current of 3.0 volts and 0.2 ampères could be maintained during the first ten minutes. As the amperage tended to fall the voltage was increased, being 3.5 volts and 0.25 ampères at the close. Rotation of cathode, moderate. Time, two hours.

The gauze disc was then washed in acidulated water, and dried carefully over a heated asbestos mat.

	Gram
Wt. Sb KCN–Na_2S method	0.2149
Wt. Sb rotating gauze cathode in CaS + $(NH_4)_2Sx$ electrolyte	0.2147
	0.2148

If conditions were not perfectly satisfactory the antimony showed a tendency to peel off from the edges of the discs, or solid particles would become embedded in the meshes of the gauze which were removed with difficulty.

Moreover, when solid stannic hydroxide was present, particles of this seemed to catch in the gauze and become reduced to metal. The tendency for tin to be deposited was also apparently greatly increased by the presence of ammonia or ammonium salts. Not all of the tin is precipitated as stannic hydroxide, even by long boiling with excess of lime if $(NH_4)_2Sx$ is present and some tin may be deposited in the presence of excess of $Ca(OH)_2$ and at boiling temperatures. Therefore a solution of CaS free from ammonium salts is required as the electrolyte, and a cathode presenting a surface upon which solid particles will not easily become attached.

An apparatus was made by the Bishop Platinum Company. A platinum cylinder 12.5 cm. in circumference and 4 cm. in height with a strong platinum stem 7 cm. in length attached to the top of the cylinder by a cross bar, formed a rotating cathode. The anode was a heavy platinum-iridium wire extending in a spiral coil (6 cm. in diameter) outside the cylinder to the bottom of the beaker and then upwards in a smaller spiral (1 cm. in diameter) inside of the cylinder. These electrodes were used in a No. 5 glass beaker, the cylinder being attached by its stem to the motor and slipped down between the anode spirals. It was found upon using the cylinder that with boiling the antimony scaled off from the bottom of the cylinder. Also that the rotation should be fairly slow.

For antimony alone the following procedure proved successful:

To 10 cc. of antimony chloride in hydrochloric acid an excess of powdered lime was added. The solution was heated and H_2S passed in at boiling. The solution was cooled and electrolyzed at 2.5 volts and 0.2 ampères = $N.D._{100}$. The voltage was raised gradually during the electrolysis till 3.5 volts was reached, the amperage being kept constant. The rotation of the cylinder was moderately slow. After two hours the cylinder was removed, washed in water acidulated with hydrochloric acid, dried over a hot plate and weighed.

	Gram
Wt. Sb, present	0.2149
Wt. Sb, found	0.2146

When the work was repeated with the addition of tin sulphides, a great many contradictory results were at first obtained. Sometimes tin was deposited and again under apparently identical conditions none would come down. The order in which the lime and hydrogen sulphide were added, the temperature and amount of boiling previous to electrolysis were found to introduce uncertain variations.

A solution of stannic chloride was precipitated with hydrogen sulphide and then boiled with excess of lime and divided into two portions. The unfiltered portion was electrolyzed at successive voltages. Above three volts a slight deposit of tin could be obtained. The filtered solution gave no deposit, even with 4.5 volts.

Again lime was added to a stannic chloride solution and well boiled, hydrogen sulphide passed in and the solution again boiled. This solution was cooled and electrolyzed with the platinum cylinder for thirty minutes at 3.0 volts. No tin was deposited. The E. M. F. was raised to 4 volts without any deposit occurring. These results are typical of a large number of apparently contradictory results.

In no case however was tin obtained from a filtered solution after boiling with excess of lime. The deposit of tin seems to be due to the reduction of solid particles of stannic hydrate which adhere to the surface of the cathode. If the stannic hydrate is in a soft colloidal form there is a great deal of this reduction, on the other hand if it is well coagulated and granular there is little tendency for it to stick or become reduced. The precipitation of the stannic hydroxide in a compact form and in a solution under conditions which are unfavorable to a gelatinous, sticky form would enable such a separation to be made successfully.

Such conditions are possible and the separation has been made successfully in several instances, but more precise experience is needed to make it a reliable separation. The best conditions so far obtained are as follows:

To a mixture of antimony and tin chlorides or sulphides pass in hydrogen sulphide and boil, add excess of powdered lime and boil. Add an excess of powdered lime to water, boil, pass in hydrogen sulphide and filter. Add this solution to the beaker containing antimony and tin sulphides as above. The solution is colorless, containing white stannic oxide. Boil ten minutes, let cool to 70° and electrolyze at 2.5 volts and 0.2 ampères $N.D._{100}$. After one hour remove the cylinder containing the antimony deposit, wash in

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acidulated water and dry over a hot plate, weigh and clean the cylinder. If any antimony remains in the solution re-insert the cylinder, add one-half gram of lime, boil, cool to 80° and electrolyze one-half hour. In this manner all the antimony may be removed from solution, in successive instalments if necessary. If the cylinder is returned to the bath without cleaning or re-weighing, the original coating may peel in spots. With an E. M. F. not above 2.75 volts the tin is never deposited from such an electrolyte. The addition of certain salts may be found particularly useful in coagulating the stannic hydroxide.

SUMMARY.

The electrolytic deposition of antimony was carefully examined in the following electrolytes with the results noted.

1. *Ammonium, sodium and barium lactates.*—Tin is not deposited from these electrolytes. Antimony may be deposited but not quantitatively. While negative evidence may possess small worth in electrolytic work, since slight modifications in some one of the many factors involved may make all the difference between failure and success, nevertheless the work upon ammonium lactate as an electrolyte was sufficiently varied to establish a strong presumption against its successful application to the determination of antimony.

2. *Ammonium polysulphide.*—The conditions for the successful deposition of antimony from this electrolyte were satisfactorily worked out. The method is novel in that it depends upon the removal or chemical change of the electrolyte during the process of electrolysis by heating. The character of the deposit of anti-

mony is very different from the dark slate-colored deposits of antimony previously obtained, being like polished platinum in appearance. Since tin may be deposited from the same electrolyte a method of determining total tin and antimony from their sulphides or chlorides is provided.

3. *Ammonium, sodium and potassium tartrates and tartaric acid.*—The results for a completely quantitative deposition of antimony were negative. A certain amount of antimony always remains in solution. Whether this amount is constant enough under given conditions to provide a means of separating tin and antimony was not finally determined.

4. *Calcium sulphide.*—Of the alkaline earth sulphides, that of calcium was shown to be best suited for the deposition of antimony. The deposits were made most successfully with rotating anodes and were of a brilliant platinum-like appearance under suitable conditions. The possibility of the separation of antimony from tin by the precipitation of the tin as stannic hydroxide and the electrolysis of the antimony from the latter in a solution of calcium sulphide was demonstrated. The method is treacherous because of the danger of reducing and depositing small amounts of the solid stannic hydroxide. With further experience it should be possible to so standardize conditions that this will always be avoided.

A fairly rapid and complete method of quantitatively determining tin and antimony with the aid of the electric current will then be available.

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